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Orientation in the Addition of HD Molecules to Buta-1,3-diene over ZnO Catalyst

A Method of Judging Heterolytic and Homolytic Dissociation of Hydrogen in Catalysis

By KEN-ICHI TANAKA* AND KAZUO AOMURA

Department of Chemistry, Faculty of Engineering, Hokkaido University,
Sapporo, Japan

AND TOSHIO OKUHARA

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo,
Hongo, Bunkyo-ku, Tokyo, Japan

AND KOSHIRO MIYAHARA

Research Institute for Catalysis, Hokkaido University, Sapporo, Japan

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Selective 1,2-addition of HD molecules to butadiene on ZnO catalyst yielded 75% of [3-$^2H_1$]but-1-ene and 25% of [4-$^2H_1$]but-1-ene. Although the adsorption of HD on ZnO prefers

$$\begin{bmatrix} \mathrm{H} & \mathrm{D} \\ | & | \\ \mathrm{Zn} & \mathrm{O} \end{bmatrix}$$

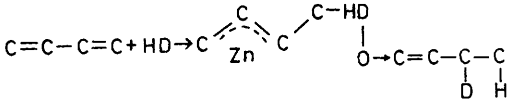
conformation at room temperature and the reverse conformation

$$\begin{bmatrix} \mathrm{D} & \mathrm{H} \\ | & | \\ \mathrm{Zn} & \mathrm{O} \end{bmatrix}$$

at −40 °C, reaction of HD at these two temperatures gave an identical ratio of [3-$^2H_1$]/[4-$^2H_1$] = 3. The dissociation of HD is in general expressed by

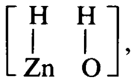
$$\mathrm{HD}\begin{cases} \xrightarrow{1} \mathrm{H(I)} + \mathrm{D(II)} \\ \xrightarrow[\beta]{} \mathrm{D(I)} + \mathrm{H(II)} \end{cases}.$$

In the case of homolytic dissociation H(I) and H(II) or D(I) and D(II) should be identical, *i.e.* $\beta = 1$, but in heterolytic dissociation it may not be unity. Provided that the hydrogen molecular identity is maintained in the hydrogenated products, the following equations were derived for n- and sec-butenyl intermediates: [3-$^2H_1$]/[4-$^2H_1$] = [$^2H_0$]$(1+\alpha\beta)$/[$^2H_2$]$(\alpha+\beta)$ for sec-butenyl and [3-$^2H_1$]/[4-$^2H_1$] = [$^2H_2$]$(\alpha+\beta)$/[$^2H_0$]$(1+\alpha\beta)$ for n-butenyl, where α is a relative rate constant of the reaction of H(I) and H(II) or D(I) and D(II) with butadiene. Accordingly, in homolytic dissociation the simple relations [3-$^2H_1$]/[4-$^2H_1$] = [$^2H_0$]/[$^2H_2$] or [$^2H_2$]/[$^2H_0$] should be established for homolytic dissociation, because $\alpha = 1$ and $\beta = 1$, whereas [3-$^2H_1$]/[4-$^2H_1$] will be equal to neither [$^1H_0$]/[$^2H_2$] nor [$^2H_2$]/[$^2H_0$] in heterolytic dissociation. It was confirmed that the hydrogenation on MoS_2 is brought about by homolytic dissociation but that on ZnO it is caused by heterolytic dissociation. A plausible mechanism assuming π-allyl anionic intermediates,



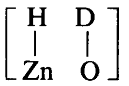
was proposed and it is explainable in terms of first-order kinetics in hydrogen pressure and the temperature-independent orientation in the 1,2-addition of HD.

Since Eishens *et al.*[1] presented spectroscopic evidence for dissociation of a hydrogen molecule on zinc oxide in the form of



$$\left[\begin{array}{cc} H & H \\ | & | \\ Zn & O \end{array}\right],$$

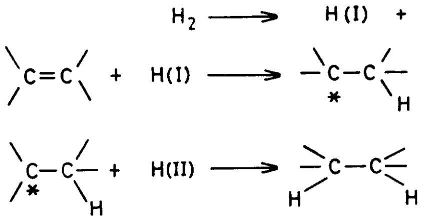
the role of this adsorption in catalysis has been a subject of interest. Kokes *et al.*[2] found that the adsorption of HD molecule on ZnO takes a preferential orientation of



$$\left[\begin{array}{cc} H & D \\ | & | \\ Zn & O \end{array}\right]$$

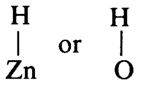
at room temperature but the reverse orientation is favoured at −40 °C.

These two types of orientation were well-explained by the thermodynamic and kinetic facilities of HD adsorption, respectively. It is known that the reaction of an olefin or diene with D_2 on a ZnO catalyst gives mainly [$^2H_2$]-adducts, that is, the molecular identity of D_2 is maintained in the products. Similar conservations of hydrogen molecular identity have been observed on oxide catalysts such as Co_3O_4,[3] Cr_2O_3,[4] CdO,[5] ZrO_2,[6] MgO,[7] ThO_2[8] and on MoS_2.[9] The hydrogenation which maintains the hydrogen molecular identity may be described in general as follows:



where H(I) and H(II) are identical in homolytic dissociation of H_2 but are different in heterolytic dissociation.

ZnO is of interest because we do not know whether



$$\begin{array}{ccc} H & & H \\ | & \text{or} & | \\ Zn & & O \end{array}$$

corresponds to H(I) in the above reaction scheme. The adsorption measurement during the hydrogenation of butadiene[10] as well of ethylene[11] on ZnO showed equilibrated adsorption of hydrogen at room temperature. If reactive intermediates of hydrogen are in adsorption equilibrium during reaction at room temperature, the hydrogenation of butadiene with HD on ZnO is expected to give different orientations at room temperature and at −40 °C.

This is not what was reported in a previous communication.[12] In this paper, the isotope effect for the addition of H_2 and D_2 as well as the orientation in the HD molecule are measured at room temperature and −40 °C and a plausible mechanism which may explain the characteristics of the hydrogenation reaction on ZnO catalyst is discussed.

EXPERIMENTAL

The hydrogenation reaction was performed in a closed circulating system with a volume of *ca.* 300 cm^3. Zinc oxide was Kadox-25 ZnO obtained from New Jersey Zinc and is the same type of zinc oxide used in the experiments of Kokes *et al.*[2]

The zinc oxide was mounted in a reactor and evacuated at *ca.* 450 °C for 4 h followed by cooling to room temperature *in vacuo*.

Ca. 0.3 g of ZnO was used for the reaction at room temperature and 1.3 g was used for the reaction at −40 °C. D_2 gas from a commercial cylinder was purified through a molecular sieve column at liquid nitrogen temperature.

Butadiene (99.5%) from Takachiho Chemicals and HD gas (98%) from Merck, Sharp and Dohme, Canada were used without further purification. Deuterated products, but-1-ene and *cis*-but-2-ene were separated by the gas chromatographic method and mass spectroscopic analysis was carried out using an ionization voltage of 12.5 eV. The locations of deuterium atoms in $[^2H_1]$but-1-ene and $[^2H_2]$but-1-ene were decided by microwave spectroscopic analysis, the details of which are described in a previous paper.[13]

A sufficient amount of *cis*-but-2-ene was accumulated by gas chromatographic separation and subjected to n.m.r. spectroscopic analysis by dissolving in carbon tetrachloride.

RESULTS

The hydrogenation of butadiene on ZnO catalyst yielded 92-95% of but-1-ene and several per cent of *cis*-but-2-ene with trace amounts of *trans*-but-2-ene at room temperature. As shown in table 1, the deuterium molecular identity was preserved in the hydrogenated products, that is, the reaction with a mixture of H_2 and D_2 gives $[^2H_0]$- and $[^2H_2]$-adducts as shown in table 1 for run E-104 and the reaction with HD gives $[^2H_1]$-adducts as shown for run E-102.

Up to the present, the preservation of deuterium molecular identity has been proved for the main product, that is, $[^2H_2]$but-1-ene takes the conformation of $[3,4\text{-}^2H_2]$but-1-ene, but little attention has been paid to minor products such as *cis*-but-2-ene and *trans*-but-2-ene.

However, it is an interesting problem to determine whether *cis*-but-2-ene is formed by 1,4-addition of hydrogen to butadiene or by consecutive isomerization of but-1-ene on ZnO.

In order to clarify this question, $[^2H_2]$*cis*-but-2-ene obtained by the reaction of butadiene with D_2 on ZnO at room temperature was subjected to n.m.r. analysis and mass spectroscopic analysis. The intensity ratio of methyl hydrogen ($—CH_3$) to olefinic hydrogen ($=CH—$) is shown in table 2. The deuterium molecular identity is entirely preserved in *cis*-but-2-ene and $(—CH_3)/(=CH_2—) = 2$ is attained. These facts indicate that *cis*-but-2-ene is formed directly by 1,4-addition of D_2 on ZnO catalyst. The isotope effects for the reaction of H_2 and D_2 with butadiene are shown in table 1 by the values of $[^2H_0]/[^2H_2]$, where the values were corrected by the H_2/D_2 ratio in the ambient gas phase, because the reaction rate is first-order in hydrogen pressures. Note that the $[^2H_0]/[^2H_2]$ ratio of but-1-ene is slightly smaller than that of *cis*-but-2-ene. This seems to indicate that the isotope effect for 1,4-addition is larger than unity although that for 1,2-addition is close to unity.

In contrast to the small isotope effect for 1,2-addition of H_2 and D_2, 1,2-addition of the HD molecule to butadiene takes a remarkable orientation which results in 73-75% of $[3\text{-}^2H_1]$but-1-ene and 27-25% of $[4\text{-}^2H_1]$but-1-ene, as shown in table 3. Note that the orientation observed in the addition of the HD molecule was exactly the same at room temperature and at −40 °C, as shown in fig. 1.

On the other hand, it has been shown that 75% of HD adsorbed on ZnO takes the conformation

$$\left[\begin{array}{cc} \mathrm{H} & \mathrm{D} \\ | & | \\ \mathrm{Zn} & \mathrm{O} \end{array}\right]$$

at room temperature but it takes the reverse conformation

$$\left[\begin{array}{cc} \mathrm{D} & \mathrm{H} \\ | & | \\ \mathrm{Zn} & \mathrm{O} \end{array}\right]$$

TABLE 1.—REACTION OF BUTADIENE WITH HD AND WITH A MIXTURE OF H_2 AND D_2 AT ROOM TEMPERATURE

	conv. (%)	but-1-ene				but-2-ene				hydrogen		
		$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$\frac{[^2H_0]}{[^2H_2]}$	$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$\frac{[^2H_0]}{[^2H_2]}$	H_2	HD	D_2
E-104	0	—	—	—	—	—	—	—	—	49.8	0.6	49.5
	5.2	47.6	4.4 (95.7)[a]	47.8	0.96	50.4	8.7	40.9	1.24	49.2	2.4	48.4
	15.7	46.1	6.5 (92.4)	47.3	0.96	49.3	10.4	40.3	1.20	47.9	5.0	47.0
	49.3	40.8	11.5 (89.6)	47.2	0.82	47.5	13.0	39.0	1.16	44.4	13.3	42.3
	72.4	38.6	15.2 (87.2)	45.6	0.77	47.4	15.1	36.8	1.17	42.8	18.2	39.0
E-104 (repeated)	0	—	—	—	—	—	—	—	—	50.6	0.7	48.7
	11.9	42.9	5.0 (93.4)	51.8	0.82	47.6	13.1	38.9	1.21	49.2	2.3	48.5
	23.0	42.0	5.4 (93.5)	52.4	0.77	46.6	10.8	41.9	1.07	48.9	3.9	47.2
	35.0	40.6	6.5 (94.0)	52.7	0.73	46.9	12.9	39.7	1.11	48.6	5.5	45.8
E-102	0	—	—	—	—	—	—	—	—	1.7	97.4	0.9
	6.6	7.2	90.4 (88.6)[a]	2.4	—	15.4	81.7 (8.8, 2.6)[b]	2.9	—	3.1	95.6	1.4
	13.0	6.6	91.0[c] (90.9)	2.3	—	13.1	83.3 (6.8, 2.3)	3.6	—	4.2	92.9	2.9
	20.6	7.4	90.9 (91.4)	2.7	—	11.3	84.5 (6.6, 2.0)	3.6	—	5.2	91.4	3.4
	26.0	—	89.8 (90.7)	2.8	—	13.1	83.4 (7.5, 1.8)	3.4	—	6.8	89.3	3.9

[a] Number in parentheses is the percentage of but-1-ene in products. [b] Numbers in parentheses are the percentage of *cis*- and *trans*-but-2-ene. [c] Sample was submitted to microwave spectroscopic analysis.

TABLE 2.—N.M.R. SPECTROSCOPIC ANALYSIS OF *cis*-BUT-2-ENE FORMED IN THE REACTION OF BUTADIENE WITH D_2 AT ROOM TEMPERATURE

time/h	conv. (%)	*cis*-but-2-ene (%)[a] $[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$[^2H_3]$	$[^2H_4]$	n.m.r. analysis $[CH_3—/—CH=]$
3.0	49.8	—	4.9	94.1	1.0	—	2.04

[a] Composition of product was 93.6% but-1-ene, 5.4% *cis*-but-2-ene and 0.9% *trans*-but-2-ene.

TABLE 3.—ORIENTATION IN THE ADDITION OF HD TO BUTADIENE ON ZnO AT ROOM TEMPERATURE AND −40 °C

						products								
	temp.	conv.	hydrogen used			but-1-ene			*cis*-but-2-ene[a]			hydrogen		
run	/°C	(%)	H_2	HD	D_2	$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	H_2	HD	D_2
101	r.t.	5.7	25.0	52.3	22.7	23.2	55.4	21.4	30.8	50.6	18.5	24.7	51.7	23.6
102	r.t.	13.0	1.7	97.4	0.9	6.6	91.0	2.3	13.1	83.3	3.6	4.2	92.9	2.9
112	−40	5.6	1.7	97.7	0.6	3.5	95.4	1.0	—	—	—	2.1	97.1	0.9

run	temp. /°C	$[^2H_1]$but-1-ene isomers $[3\text{-}^2H_1]$but-1-ene	$[4\text{-}^2H_1]$but-1-ene
101	r.t.	72.8	27.2
102	r.t.	75.4	24.6
112	−40	75.2	24.8

[a] Fraction of *cis*-but-1-ene in products was 10% in run 101 and 9.1% in run 102.

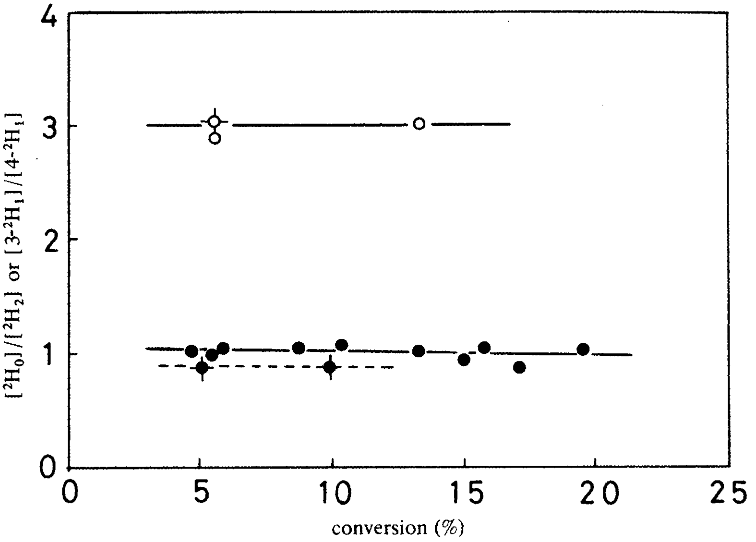
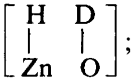


FIG. 1.—Isotope effect for 1,2-addition of H_2 and D_2 in the reaction with 1,3-butadiene on ZnO and the orientation in the reaction of butadiene with HD. ○, -⌖-; $[3\text{-}^2H_1]$but-1-ene/$[4\text{-}^2H_1]$but-1-ene at room temperature and −40 °C. ●, -✦-; $[^2H_0]$but-1-ene/$[^2H_2]$but-1-ene at room temperature and −40 °C.

at −40 °C. This suggests that the orientation in 1,2-addition of HD to butadiene brought about on ZnO catalyst is not caused by a thermodynamically favourable conformation as



$$\left[\begin{array}{cc} \mathrm{H} & \mathrm{D} \\ | & | \\ \mathrm{Zn} & \mathrm{O} \end{array}\right];$$

in other words, the hydrogen which undergoes the hydrogenation reaction might not be in adsorption equilibrium during the hydrogenation reaction at room temperature.

DISCUSSION

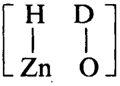
Dent and Kokes[14] classified adsorbed hydrogen on ZnO into two types, type-I and type-II adsorptions. Type-I adsorption is reversible at room temperature and approaches a saturation value at pressures of *ca.* 30-40 Torr hydrogen. This type of adsorption gives i.r. absorption spectra.

In contrast to type-I adsorption, type-II adsorption is irreversible and is inactive for i.r. absorption spectra. The reactivity of these two types of hydrogen infer that type-I hydrogen is a reactive species for the catalytic hydrogenation reaction but type-II is inert. However, Baranski and Cvetanovic[15] have pointed out that the reactive hydrogen is a part of type-I adsorption.

Furthermore, the discrepancy between the kinetics of hydrogen pressure dependence and the amount of type-I adsorption during the reaction has been noted in the hydrogenation of butadiene[10] as well as in the hydrogenation of ethylene.[11]

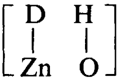
That is, type-I hydrogen is in adsorption equilibrium during the hydrogenation reaction at room temperature and approaches a saturated adsorption at high pressures of hydrogen, whereas the hydrogenation of butadiene has a first-order dependence on hydrogen pressure and that of ethylene has a half-order dependence on hydrogen pressure.

On the other hand, the adsorption of HD at room temperature takes the thermodynamically preferential conformation of



$$\left[\begin{array}{cc} \mathrm{H} & \mathrm{D} \\ | & | \\ \mathrm{Zn} & \mathrm{O} \end{array}\right]$$

but the adsorption at −40 °C favours the reverse conformation,



$$\left[\begin{array}{cc} \mathrm{D} & \mathrm{H} \\ | & | \\ \mathrm{Zn} & \mathrm{O} \end{array}\right]$$

by reason of kinetic facility.[2] Accordingly, if type-I hydrogen is involved in the hydrogenation reaction of butadiene, the reaction of butadiene with HD may take a reverse orientation at room temperature and −40 °C, because the type-I hydrogen is in adsorption equilibrium at room temperature but not at −40 °C. Contrary to our expectation, the hydrogenation of butadiene with HD at room temperature and −40 °C gave an identical ratio of [3-^{2}H$_1$]but-1-ene/[4-^{2}H$_1$]but-1-ene = 3, as was reported in a previous communication.[12] Catalytic hydrogenation of unsaturated hydrocarbons requires the dissociation of the hydrogen molecule in either a homolytic or a heterolytic manner.

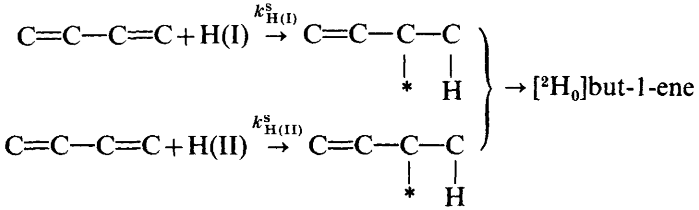
However, so far no method for ascertaining either homolytic or heterolytic dissociation in the hydrogenation reaction has been proposed and a method which might be the first promising one for this purpose is proposed in this paper.

Dissociation of H_2, D_2 and HD molecules on catalysts are described in general as follows:

$$\mathrm{H_2 \rightarrow H(I) + H(II)}$$
$$\mathrm{D_2 \rightarrow D(I) + D(II)}$$
$$\mathrm{HD}\left\{\begin{array}{l} \xrightarrow{1} \mathrm{H(I) + D(II)} \\ \xrightarrow[\beta]{} \mathrm{D(I) + H(II)} \end{array}\right.$$

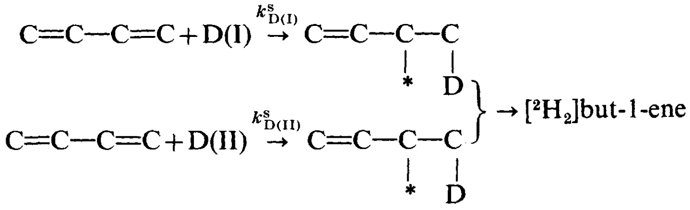
where the amount of each species is related by the following relations: $[\mathrm{H(I)}] = [\mathrm{H(II)}]$ and $[\mathrm{D(I)}] = [\mathrm{D(II)}]$ for H_2 and D_2, $[\mathrm{H(I)}] = [\mathrm{D(II)}]$ and $[\mathrm{H(I)}]/[\mathrm{H(II)}] = 1/\beta$ for HD. Provided that the hydrogenation reaction of butadiene proceeds stepwise, the reaction with H_2, D_2 and HD *via* sec-butenyl intermediates can be described as follows:

(1) H_2



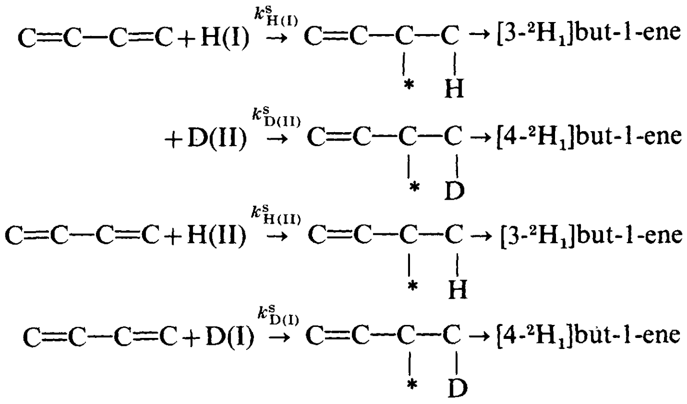
$$\left.\begin{array}{l} \mathrm{C{=}C{-}C{=}C + H(I)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{H(I)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{H}{C}} \\ \mathrm{C{=}C{-}C{=}C + H(II)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{H(II)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{H}{C}} \end{array}\right\} \rightarrow [^2\mathrm{H_0}]\text{but-1-ene}$$

(2) D_2



$$\left.\begin{array}{l} \mathrm{C{=}C{-}C{=}C + D(I)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{D(I)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{D}{C}} \\ \mathrm{C{=}C{-}C{=}C + D(II)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{D(II)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{D}{C}} \end{array}\right\} \rightarrow [^2\mathrm{H_2}]\text{but-1-ene}$$

(3) HD



$$\mathrm{C{=}C{-}C{=}C + H(I)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{H(I)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{H}{C}} \rightarrow [3\text{-}^2\mathrm{H_1}]\text{but-1-ene}$$
$$+\mathrm{D(II)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{D(II)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{D}{C}} \rightarrow [4\text{-}^2\mathrm{H_1}]\text{but-1-ene}$$
$$\mathrm{C{=}C{-}C{=}C + H(II)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{H(II)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{H}{C}} \rightarrow [3\text{-}^2\mathrm{H_1}]\text{but-1-ene}$$
$$\mathrm{C{=}C{-}C{=}C + D(I)} \xrightarrow{k^{\mathrm{s}}_{\mathrm{D(I)}}} \mathrm{C{=}C{-}\underset{*}{C}{-}\underset{D}{C}} \rightarrow [4\text{-}^2\mathrm{H_1}]\text{but-1-ene}$$

where $k^{\mathrm{s}}_{\mathrm{H(I)}}$, $k^{\mathrm{s}}_{\mathrm{H(II)}}$, $k^{\mathrm{s}}_{\mathrm{D(I)}}$ and $k^{\mathrm{s}}_{\mathrm{D(II)}}$ are the rate constants for the formation of sec-butenyl intermediates. In conformity with the fact that the hydrogen molecular identity is preserved in the hydrogenated products, the rate determining step might be assumed to be the formation of either n- or sec-butenyl species. In the case of sec-butenyl intermediates, the ratio $[^2\mathrm{H_0}]/[^2\mathrm{H_2}]$ for but-1-ene in the reaction with H_2 and D_2 is given by the following equation:

$$\frac{[^2\mathrm{H_0}]\text{but-1-ene}}{[^2\mathrm{H_2}]\text{but-1-ene}} = \frac{k^{\mathrm{s}}_{\mathrm{H(I)}}[\mathrm{H(I)}] + k^{\mathrm{s}}_{\mathrm{H(II)}}][\mathrm{H(II)}]}{k^{\mathrm{s}}_{\mathrm{D(I)}}[\mathrm{D(I)}] + k^{\mathrm{s}}_{\mathrm{D(II)}}[\mathrm{D(II)}]}$$
$$= \frac{[k^{\mathrm{s}}_{\mathrm{H(I)}} + k^{\mathrm{s}}_{\mathrm{H(II)}}][\mathrm{H(I)}]}{[k^{\mathrm{s}}_{\mathrm{D(I)}} + k^{\mathrm{s}}_{\mathrm{D(II)}}][\mathrm{D(I)}]} = \frac{k^{\mathrm{s}}_{\mathrm{H(I)}}(1+\alpha)[\mathrm{H(I)}]}{k^{\mathrm{s}}_{\mathrm{D(I)}}(1+\alpha)[\mathrm{D(I)}]} = \frac{k^{\mathrm{s}}_{\mathrm{H(I)}}}{k^{\mathrm{s}}_{\mathrm{D(I)}}}$$

where $$\frac{k^{\mathrm{s}}_{\mathrm{H(I)}}}{k^{\mathrm{s}}_{\mathrm{H(II)}}} = \frac{k^{\mathrm{s}}_{\mathrm{D(I)}}}{k^{\mathrm{s}}_{\mathrm{D(II)}}} = \frac{1}{\alpha}$$

and H(I) = H(II) may be satisfactory approximations.

In the reaction with HD molecule, the ratio of [3-$^2H_1$]but-1-ene to [4-$^2H_1$]but-1-ene is described by the following equation:

$$\frac{[3\text{-}^2\mathrm{H}_1]\text{but-1-ene}}{[4\text{-}^2\mathrm{H}_1]\text{but-1-ene}} = \frac{k^{\mathrm{s}}_{\mathrm{H(II)}}[\mathrm{H(II)}]+k^{\mathrm{s}}_{\mathrm{H(I)}}[\mathrm{H(I)}]}{k^{\mathrm{s}}_{\mathrm{D(I)}}[\mathrm{D(I)}]+k^{\mathrm{s}}_{\mathrm{D(II)}}[\mathrm{D(II)}]}$$

$$= \frac{k^{\mathrm{s}}_{\mathrm{H(I)}}(1+\alpha\beta)}{k^{\mathrm{s}}_{\mathrm{D(I)}}(\alpha+\beta)} = \frac{[^2\mathrm{H}_0](1+\alpha\beta)}{[^2\mathrm{H}_2](\alpha+\beta)}$$

where β indicates the orientation in the adsorption of HD and α is relative reactivity of H(I) and H(II) or D(I) and D(II) with butadiene to form sec-butenyl intermediates; H(I)/H(II) = D(I)/D(II) = $1/\beta$ and $k^{\mathrm{s}}_{\mathrm{H(I)}}/k^{\mathrm{s}}_{\mathrm{H(II)}} = k^{\mathrm{s}}_{\mathrm{D(I)}}/k^{\mathrm{s}}_{\mathrm{D(II)}} = 1/\alpha$. In the same way, the following relations can be derived for n-butenyl intermediates:

$$\frac{[^2\mathrm{H}_0]\text{but-1-ene}}{[^2\mathrm{H}_2]\text{but-1-ene}} = \frac{k^{\mathrm{n}}_{\mathrm{H(I)}}}{k^{\mathrm{n}}_{\mathrm{D(I)}}} \text{ and } \frac{[3\text{-}^2\mathrm{H}_1]\text{but-1-ene}}{[4\text{-}^2\mathrm{H}_1]\text{but-1-ene}} = \frac{[^2\mathrm{H}_2](\alpha+\beta)}{[^2\mathrm{H}_0](1+\alpha\beta)}.$$

In the case of homolytic dissociation of hydrogen, $\beta = 1$ and $\alpha = 1$ should be established. As a result, a simple relation will be established between [$^2H_0$]/[$^2H_2$] and [3-$^2H_1$]/[4-$^2H_1$] as follows:

(1) in the case of n-butenyl intermediates,

$$\frac{[3\text{-}^2\mathrm{H}_1]\text{but-1-ene}}{[4\text{-}^2\mathrm{H}_1]\text{but-1-ene}} = \frac{[^2\mathrm{H}_2]\text{but-1-ene}}{[^2\mathrm{H}_0]\text{but-1-ene}}$$

(2) in the case of sec-butenyl intermediates,

$$\frac{[3\text{-}^2\mathrm{H}_1]\text{but-1-ene}}{[4\text{-}^2\mathrm{H}_1]\text{but-1-ene}} = \frac{[^2\mathrm{H}_0]\text{but-1-ene}}{[^2\mathrm{H}_2]\text{but-1-ene}}.$$

In the hydrogenation of butadiene and of α-olefins on MoS_2 catalyst, one of above relations, [3-$^2H_1$]/[4-$^2H_1$] = [$^2H_0$]/[$^2H_2$], was established as shown in fig. 2,[13, 16, 17] which may prove homolytic dissociation of hydrogen giving dihydride sites. A similar result was obtained on MoO_x/TiO_2.[18] In heterolytic dissociation, however, the ratio [3-$^2H_1$]/[4-$^2H_1$] will agree with neither the values of [$^2H_0$]/[$^2H_2$] nor [$^2H_2$]/[$^2H_0$]. The hydrogenation of butadiene on ZnO seems to be a typical case of heterolytic dissociation, because the reaction with HD takes a remarkable orientation but the isotope effect is small as shown in fig. 1 and in table 3. Taking into account the facts that the orientation of the adsorption of HD on ZnO takes an equilibrium conformation at room temperature but is not in equilibrium at −40 °C,[2] the dissociated hydrogen which undergoes the reaction with butadiene may not be in equilibrium orientation in adsorption during the reaction, although the type-I hydrogen is in adsorption equilibrium during the reaction.[10, 11]

But-1-ene, as well as but-2-ene, is adsorbed on ZnO in the form of a π-allyl anionic species by losing a proton. In agreement with similar structural conformations for the intermediates of the hydrogenation of butadiene and the intermediates of the isomerization of n-butenes on ZnO, a plausible mechanism which satisfies the following characteristics is proposed. (1) first-order dependence on hydrogen pressures in a pressure range giving saturation of the type-I adsorption; (2) the 1,2-addition of HD takes a temperature-independent orientation, although the adsorption of HD on ZnO shows temperature-dependent conformations; (3) a π-allyl anionic species is one of the most probable intermediates.

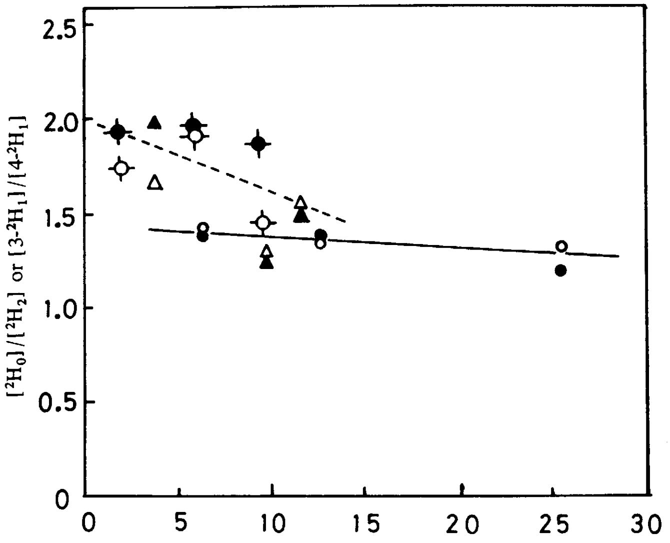
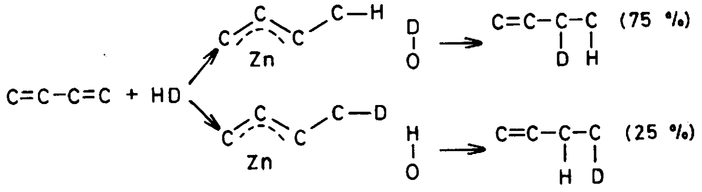


FIG. 2.—Orientation in the addition of HD to butadiene and to α-olefins and isotope effects for the addition of H_2 and D_2 on MoS_2 catalyst at room temperature. Butadiene: ○, $[^2H_0]/[^2H_2]$; ●, $[3\text{-}^2H_1]/[4\text{-}^2H_1]$. Propene: ⌖, $[^2H_0]/[^2H_2]$; ◆, $[2\text{-}^2H_1]/[1\text{-}^2H_1]$. But-1-ene: △, $[^2H_0]/[^2H_2]$; ▲, $[2\text{-}^2H_1]/[1\text{-}^2H_1]$.



In the above scheme, the activation process of the hydrogen molecule is analogous to that on CdO, that is, CdO has no catalytic activity for the H_2–D_2 equilibration as well as for the hydrogenation of olefins, but the adsorbed conjugated diene on CdO promotes heterolytic dissociation of the hydrogen molecule by forming π-allyl anions.[5]

It was confirmed that the type-I adsorption and the adsorption of ethylene compete for the same sites on ZnO.[11] Taking into account the slow H_2–D_2 equilibration in the presence of butadiene, the sites for the type-I adsorption are almost entirely occupied by butadiene and the heterolytic dissociation of hydrogen molecule is brought about in a similar manner as was observed on CdO. 1,4-addition, giving but-2-ene is a minor contribution in the hydrogenation of butadiene on ZnO catalyst, as shown in table 2. However, it is obvious that 1,4-addition on ZnO favours *cis*-but-2-ene formation. As we have suggested in previous papers,[5, 19] π-allylic anion intermediates bring about both 1,2- and 1,4-additions in the reaction of conjugated dienes and the relative contributions of these two types of addition depend on the kinetic facility caused by surfaces.

In fact, π-allyl anions formed on CdO bring about *ca.* 55% 1,2-addition but the π-allyl anion on ZnO reacts predominantly to give 1,2-addition. In contrast to this selectivity, the *cis*/*trans* ratio in the 1,4-addition depends on the barrier to internal rotation of π-allyl intermediates and π-allyl anionic intermediates give, in general, a large *cis*/*trans* ratio. These facts may support the above mechanism in which preferential 1,2-addition of butadiene in ZnO occurs *via* π-allyl anionic intermediates which are formed by the heterolytic dissociation of a hydrogen molecule with adsorbed butadiene on ZnO. Isotope effects for the 1,2- and 1,4-addition in table 1 are of a different magnitude; however, such a difference is unexpected from our mechanism. This might be caused by the heterogeneity of the ZnO surface, that is, the intermediate to 1,4-addition might take slightly different values of $k^{\S}_{\mathrm{H(I)}}/k^{\S}_{\mathrm{D(I)}}$ and/or H(I)/D(I). The present workers consider that this problem remains to be solved.

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[1] R. P. Eishens, W. A. Pliskin and M. S. D. Low, *J. Catal.*, 1962, **1**, 180.

[2] R. J. Kokes, A. L. Dent, C. C. Chang and L. T. Dixon, *J. Am. Chem. Soc.*, 1972, **94**, 4429.

[3] K. Tanaka, H. Nihira and A. Ozaki, *J. Phys. Chem.*, 1970, **74**, 4510.

[4] R. L. Burwell Jr, A. B. Littlewood, M. Cardew, G. Pass and C. T. H. Stoddart, *J. Am. Chem. Soc.*, 1960, **82**, 6272.

[5] T. Okuhara and K. Tanaka, *J. Catal.*, 1980, **61**, 135.

[6] Y. Yamaguchi and J. Hightower, *J. Am. Chem. Soc.*, 1976, **99**, 4201.

[7] H. Hattori, Y. Tanaka and K. Tanabe, *J. Am. Chem. Soc.*, 1976, **98**, 4652.

[8] Y. Imizu, K. Tanabe and H. Hattori, *J. Catal.*, 1979, **56**, 303.

[9] T. Okuhara and K. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1976, 42.

[10] S. Naito, Y. Sakurai, H. Shimizu, T. Onishi and K. Tamaru, *Bull. Chem. Soc. Jpn*, 1970, **43**, 2274; *Trans. Faraday Soc.*, 1971, **67**, 1529.

[11] K. Tanaka and G. Blyholder, *J. Phys. Chem.*, 1972, **76**, 1394.

[12] T. Okuhara, T. Kondo and K. Tanaka, *J. Phys. Chem.*, 1977, **81**, 808.

[13] T. Okuhara and K. Tanaka, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 7, 1403.

[14] A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, 1969, **73**, 3772, 3781.

[15] A. Baranski and R. J. Cvetanovic, *J. Phys. Chem.*, 1971, **75**, 208.

[16] T. Okuhara and K. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1976, 199; T. Okuhara, T. Kondo and K. Tanaka, *Chem. Lett.*, 1976, 717.

[17] K. Tanaka and T. Okuhara, *Catal. Rev.* 1977, **15**, 249.

[18] K. Tanaka, K. Tanaka and K. Miyahara, *Chem Lett.*, 1978, 943.

[19] K. Tanaka and T. Okuhara, *J. Catal.*, 1980, **65**, 1.

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